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Collision-Induced Absorption in the $a^1\Delta_g(v'=0) \leftarrow X^3\Sigma_g^-(v=0)$ Transition in O_2–CO_2, O_2–N_2, and O_2–H_2O Mixtures

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When O_2 is perturbed by collisions with other molecules, the weak spin-forbidden magnetic dipole transition $a^1\Delta_g \leftarrow X^3\Sigma_g^-$ shows a broad continuum absorption underlying the sharp lines. This collision-induced enhancement absorption plays a role in the Earth's atmosphere and much experimental work has been carried out to measure the binary absorption coefficient with different perturber gases. Recent work on the $v'=0 \leftarrow v=0$ band in O_2–CO_2 mixtures yielded a value for the coefficient that was approximately three times that of earlier measurements on O_2–N_2 mixtures. In the present note, we calculate the absorption theoretically assuming that the long-range quadrupole-induced dipole mechanism is dominant. Using experimental polarizability matrix elements of CO_2 and *ab initio* results in the literature for the quadrupolar transition matrix element for O_2, we find good agreement for O_2–CO_2 mixtures without any adjustable parameters. The agreement for O_2–N_2 is less good, and because of the much smaller polarizability of N_2 than of CO_2, we suggest that one has to include a short-range component in addition to the long-range one treated here. We also calculate the binary absorption coefficient for O_2–H_2O, for which no experimental data are available, and we synthesize the corresponding spectrum for use in atmospheric modeling.

I. INTRODUCTION

The collision-induced fundamental band of oxygen is important from a historical as well as a practical viewpoint, because of the absorption in long-path measurements through the Earth's atmosphere (*1, 2*). Historically, this was the system in which collision-induced absorption (CIA) was first identified by Welsh and co-workers in 1949 (*3*). Not long after, the enhancement in the $a \leftarrow X$ electronic transition was observed. In the intervening years, this absorption has been seen in the solid (*4*), liquid (*5*), and gaseous phases (*6–10*) with a variety of perturbers. For an overview of collision-induced absorption, the reader is referred to the excellent monograph by Frommhold (*11*).

During this period, there have also been a large number of *ab initio* works calculating the spin-forbidden magnetic dipole and electric quadrupole transition matrix elements arising from spin–orbit mixing of the low-lying electronic states (*12–14*). Although the sharp lines of the $a \leftarrow X$ transition in the low-pressure gas are dominated by the magnetic dipole mechanism, it will be shown later that the broad CIA spectrum is dominated by the quadrupole-induced dipole mechanism.

In Section II, we first briefly review the theoretical calculation of the binary enhancement coefficient for the isotropic and anisotropic quadrupolar mechanisms. We then give the details of the calculations for O_2–CO_2 and O_2–N_2 and compare our results to the recent, most accurate experimental results. In Section III, we discuss the conclusions of the present study and the modifications necessary to obtain improved agreement for the O_2–N_2 and O_2–O_2 cases. Finally, we apply the theory to O_2–H_2O for which no experimental data exist, and by assuming a normalized lineshape similar to that calculated for other molecular systems, we calculate a synthetic spectrum for absorption in the $v'=0 \leftarrow v=0$ spectral region. This will enable one to assess the importance of the CIA in atmospheric processes.

II. THEORY

Because the theory for the isotropic and anisotropic quadrupolar contributions to the binary absorption coefficient has been published previously (*15–18*), we give here only the relevant results. Neglecting the small J-dependence of the matrix elements, one can obtain from the work of Poll and Hunt (*19*) the following expression in units of cm^{-2} $amagat^{-2}$ for the integrated intensity of the isotropic contribution for O_2–P ($P = CO_2$, N_2, or H_2O) mixtures:

$$\frac{\int A(\omega)\, d\omega}{\rho_{O_2}\rho_P} = 4\pi^2\alpha_F n_0^2 a_0^5 \langle 0|\alpha_P|0\rangle^2 \langle a|Q|X\rangle_{00}^2 I(6)\bar{\omega}_{iso}. \quad [1]$$

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TABLE 1
Molecular Data Used for the Calculations

Parameter	Molecule O_2	CO_2	N_2	H_2O
σ (a_0)	6.55[a]	7.842[b]	6.956[d]	6.50[e]
ϵ/k (K)	106.7[a]	190[b]	91.5[d]	335[e]
$\langle 0\|\alpha_P\|0\rangle$ (a_0^3)	10.87[a]	17.81[c]	11.74[d]	9.92[e]
$\langle 0\|\gamma_P\|0\rangle$ (a_0^3)	7.30[a]	13.99[c]	4.75[d]	-0.024[c]
$\langle 0\|Q\|0\rangle$ (ea_0^2)	−0.264[a]	−3.197[c]	—	—
$\langle a\|Q\|X\rangle$ (ea_0^2)	2.09×10^{-2}	—	—	—
System:	O_2-CO_2	O_2-N_2	O_2-H_2O	
σ (a_0)	7.196	6.753	6.525	
ϵ/k (K)	142.4	98.8	189	
I(6) $\times 10^{-4}$	2.15	2.86	3.73	
$\bar{\omega}_{iso}$	7885	7885	7885	
$\bar{\omega}_{aniso}$	7886	7892	—	

[a] Ref. (*16*).
[b] Ref. (*20*).
[c] Ref. (*21*).
[d] Ref. (*15*).
[e] Ref. (*22*).

In this expression, ρ_{O_2} and ρ_P are the densities in amagat,[2] $A(\omega)$ is the absorption coefficient in cm^{-1} at frequency ω (cm^{-1}), and the integral is taken over the extent of the (0, 0) band from approximately 7780 to 8080 cm^{-1}. α_F is the fine structure constant, n_0 is the number density at standard temperature and pressure, a_0 is the Bohr radius, and $I(6)$ is the dimensionless integral

$$I(6) = 4\pi \int_0^\infty \exp[-V_{iso}(x)/kT] x^{-6}\, dx, \qquad [2]$$

where $x \equiv R/a_0$. We have approximated the pair distribution function $g(R)$ by the classical limit, $\exp(-V_{iso}(x)/kT)$, where $V_{iso}(x)$ is the isotropic interaction potential between O_2 and P. The integral can be calculated using a Lennard–Jones model for $V_{iso}(x)$ with the parameters ϵ/k and σ calculated using the usual combining rules. The numerical values used are listed in Table 1. The factor $\bar{\omega}_{iso}$ is the intensity-weighted transition frequency

$$\bar{\omega}_{iso} = \sum_{J,J'} \omega_{J,J'} P_J C(J2J';00)^2, \qquad [3]$$

where the quadrupole transition frequencies for the $a \leftarrow X$ band can be approximated from the known spectroscopic constants (*23*); $C(J2J';00)$ is a Clebsch-Gordan coefficient, and the P_J are the normalized Boltzmann factors

$$P_J = \frac{g_J \exp(-E_{rot}/kT)}{\sum_J g_J \exp(-E_{rot}/kT)}, \qquad [4]$$

where g_J are the statistical weights. The numerical value of $\bar{\omega}_{iso}$ is close to the band-center frequency, $\omega_{00} = 7880$ cm^{-1}, as can be seen from the value listed in Table 1. The values for the isotropic polarizability matrix elements for the three perturbers are also listed in Table 1. The quadrupole transition moment $\langle a|Q|X\rangle_{00}$ is obtained from *ab initio* calculation by Minaev (*24*) $\langle a|Q|X\rangle = 2.1 \times 10^{-2}$ ea_0^2 multiplied by the square root of the Franck–Condon factor for the $v' = 0 \leftarrow v = 0$ transition (0.9934) (*23*), giving the result listed in Table 1. Using these values, we obtain for the binary absorption coefficient from the isotropic quadrupole mechanism the values 2.04×10^{-4} cm^{-2} $amagat^{-2}$ for O_2–CO_2 and 1.18×10^{-4} for O_2–N_2.

For the anisotropic quadrupolar mechanism, there are three components (*25*), whose squares add incoherently. Following the same procedure as above, we obtain the expression for the contribution to the binary absorption coefficient

$$\frac{\int A(\omega)\, d\omega}{\rho_{O_2}\rho_P} = \frac{4\pi^2}{3}\alpha_F n_0^2 a_0^5 I(6)\bar{\omega}_{aniso} \times \left[\frac{2}{3}\langle 0|\gamma_P|0\rangle^2\langle a|Q|X\rangle^2 + \frac{2}{3}\langle 0|Q_P|0\rangle^2\langle a|\gamma|X\rangle^2 - \frac{4}{5}\langle 0|Q_P|0\rangle\langle a|Q|X\rangle\langle 0|\gamma_P|0\rangle\langle a|\gamma|X\rangle\right], \qquad [5]$$

where

$$\bar{\omega}_{aniso} = \sum_{J_1,J_1'} P_{J_1} C(J_1 2 J_1';00)^2 \sum_{J_2,J_2'} P_{J_2} C(J_2 2 J_2';00)^2 \times (\omega_{J_1 J_1'}(P) + \omega_{00} + \omega_{J_2 J_2'}(O_2)). \qquad [6]$$

In this expression, J_1 and J_1' are the initial and final rotational quantum numbers for the pure rotational transition in the perturber gas P, J_2 and J_2' are the corresponding rotational quantum numbers in O_2, and ω_{00} is the band center frequency; the "00" subscript on the $a \leftarrow X$ matrix elements has been suppressed. The values obtained for $\bar{\omega}_{aniso}$ are listed in Table 1.

In principle, the value for the $a \leftarrow X$ matrix element of the anisotropic polarizability, γ, can be obtained experimentally from a measurement of the depolarized Raman intensity, or from *ab initio* calculations. To the best of our knowledge, this is not known. For CO_2 because the value of the anisotropic polarizability is large and comparable to the isotropic polarizability, we calculate the contribution only from the first term in Eq. [5]. We obtain 2.8×10^{-5} cm^{-2} $amagat^{-2}$, which when added to the isotropic result yields the theoretical value 2.32×10^{-4} cm^{-2} $amagat^{-2}$. This value is in very good agreement with the experimental result $2.13(29) \times 10^{-4}$ cm^{-2} $amagat^{-2}$ (*26*). The two terms in Eq. [5] which we neglected may either add or subtract from the first term, depending on the sign of the unknown $\langle a|\gamma|X\rangle$ matrix element. In any case, because the anisotropic contributions are typically an order of magnitude less than the isotropic contributions (*15–17*), we expect that the neglect of these two terms will not substantially change the agreement obtained above.

[2] The dimensionless unit amagat is defined as the ratio of the measured density to the density of the standard atmosphere.

III. DISCUSSION AND CONCLUSIONS

Because of the large σ and isotropic polarizability matrix element of CO_2, one would expect that the long-range isotropic induction mechanism considered above would dominate. This assertion is supported by the good numerical agreement obtained between theory and experiment. We note that there is an additional additive isotropic contribution to the binary absorption coefficient whose magnitude is given by

$$\left[\frac{\langle a|\alpha_{O_2}|X\rangle\langle 0|Q_{CO_2}|0\rangle}{\langle a|Q_{O_2}|X\rangle\langle 0|\alpha_{CO_2}|0\rangle}\right]^2 2.30\times 10^{-4} = 1.7\times 10^{-2}\langle a|\alpha_{O_2}|X\rangle^2. \quad [7]$$

As noted above, the two anisotropic quadrupolar contributions (see Eq. [5]) proportional to $\langle a|\gamma|X\rangle$ and $\langle a|\gamma|X\rangle^2$ have also been neglected. However, one would expect that all these contributions would be small vis-a-vis the isotropic contribution calculated. These additional contributions can easily be included if absolute Raman intensity measurements or *ab initio* calculations for the polarizability matrix elements become available.

For O_2–N_2, the theoretical value is a factor 1.7 times greater than the observed value (*10*). It is unlikely that the neglected contributions discussed above can account for this discrepancy. Because both $\langle 0|\alpha_{N_2}|0\rangle$ and σ are smaller in this case, one would expect that short-range contributions neglected in the analysis above could result in appreciable absorption. As in the case of the fundamental CIA absorption (*17*), one could model this by including a short-range component in the induced dipole having the same symmetry; that is,

$$\mu \propto \left[\langle a|Q|X\rangle\langle 0|\alpha_P|0\rangle R^{-4} \pm \mu_2 e^{-[(R-\sigma)/\rho]}\right], \quad [8]$$

where ρ is a range parameter and μ_2 is an adjustable strength. Since the absorption depends on the square of the dipole, the interference between the long- and short-range parts can either increase or decrease the value obtained from the long-range part alone. In the fundamental band, we have

found previously by simultaneously fitting O_2–O_2, O_2–N_2, N_2–O_2, and N_2–N_2 results (where the first molecule makes the vibrational transition) and all the long-range matrix elements are known, that in order to obtain agreement, we had to introduce a short-range component which had a similar value but a different sign for O_2–N_2 and N_2–O_2 (*17*).

In the present case, there are a number of additional data that indicate the need to include short-range effects. First, the observed O_2–O_2 binary absorption coefficient is larger than that of O_2–N_2 by a factor of approximately 5 (*10*), whereas the ratio at 300 K,

$$\frac{\langle 0|\alpha_{O_2}|0\rangle^2 I_{O_2-O_2}(6)}{\langle 0|\alpha_{N_2}|0\rangle^2 I_{O_2-N_2}(6)} \approx 1, \quad [9]$$

cannot explain the observed difference. The interference term, if destructive for O_2–N_2 and constructive for O_2–O_2, could partially account for the observed difference.

Second, the observed binary absorption coefficients for the $(v'=1\leftarrow v=0)$ and $(v'=0\leftarrow v=1)$ vibrational bands of the $a\leftarrow X$ transition have values which are comparable to those of the $(v'=0\leftarrow v=0)$ band considered in the present paper. This is inconsistent with the Franck–Condon factors for these transitions, and had lead to the speculation that one must include short-range overlap effects (*9*).

Finally, the observed increase in the binary absorption coefficient for O_2–O_2 as the temperature decreases is larger than that expected from the ratio of $I_{100\,K}(6)/I_{300\,K}(6)=1.4$ from the present formulation versus 1.55 from experiment (*9*), implying a stronger dependence of the induced dipole moment on the separation than the R^{-4} from the long-range quadrupolar part.

Because of the present lack of knowledge of the polarizability matrix elements, mainly $\langle a|\,\gamma\,|X\rangle$, and the significant discrepancies among the previous experimental measurements for O_2–O_2 and O_2–N_2, we feel that it is not worthwhile at present to introduce adjustable parameters (μ_2 and ρ) in order to force agreement.

Finally, we consider the case of O_2–H_2O, because this system would account for the greatest variability of CIA in the Earth's atmosphere in the 1.27-μm region. Using the theory outlined in Section 2 and the results from Table 1, the binary absorption coefficient from the isotropic quadrupole mechanism is 1.09×10^{-4} cm^{-2} amagat^{-2} for O_2–H_2O. Again, only approximate theoretical results are possible, because one would expect significant short-range effects for this system as well, given the smaller σ. Nevertheless, it is clear from the ratio R of the integrated intensity for O_2–H_2O (ignoring the anisotropic quadrupolar contribution, which is very small due to the smallness of γ for H_2O) to that for O_2–CO_2, $R=0.474\,\rho_{H_2O}/\rho_{CO_2}$, that under most atmospheric conditions, the CIA of O_2–H_2O is more important than that of O_2–CO_2. In addition to the quadrupolar contribution to the CIA, the allowed dipole of H_2O would contribute additively to the CIA primarily through the isotropic dipolar mechanism, where the dipole-induced dipole absorption is

$$\int A(\omega)\,d\omega \propto I(4)\langle 0|\mu_{H_2O}|0\rangle^2\langle a|\alpha|X\rangle^2. \quad [10]$$

If we consider the ratio of the integrated absorption intensity for the dipole-induced dipole mechanism ($\overline{A}^{DID}$) to that for the presently calculated quadrupole-induced dipole mechanism

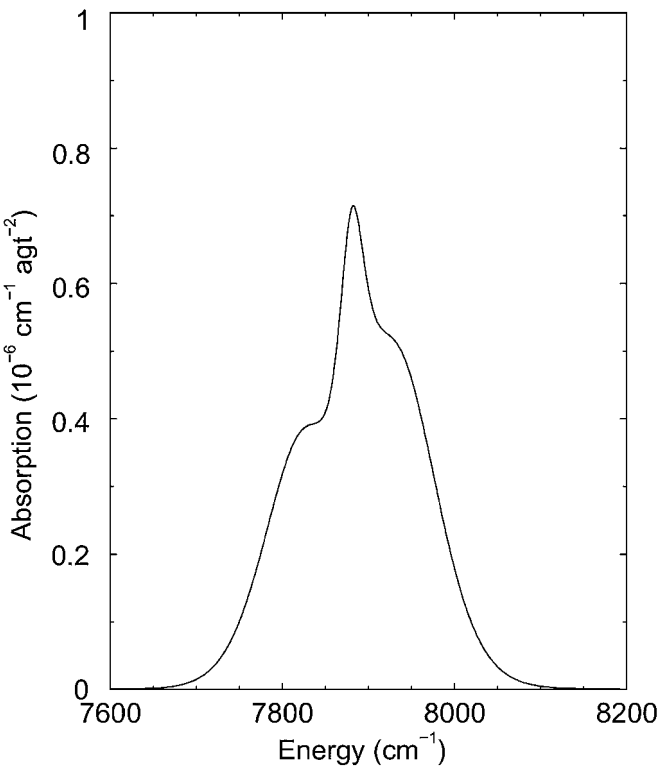

FIG. 1. The absorption $A(\omega)/(\rho_{O_2}\rho_{H_2O})$ in units of 10^{-6} cm^{-1} amagat^{-2} versus the frequency ω (cm^{-1}) at T = 296 K.

$(\bar{A}^{QID})$, we obtain

$$\frac{\bar{A}^{DID}}{A^{QID}} \approx 1.6 \times 10^2 \langle a|\alpha|X\rangle^2. \qquad [11]$$

Clearly, the relative importance of the dipole-induced dipole mechanism depends strongly on the matrix element $\langle a|\alpha|X\rangle$. However, the value of the matrix element of α, as well as that for the anisotropic polarizability $\langle a|\gamma|X\rangle$, is not known and difficult to estimate accurately. The theoretical results can easily be refined if these values become available.

In order to assess the importance of the CIA for O_2–H_2O (utilizing the known isotropic quadrupole-induced dipole mechanism only), we use the theoretically determined binary absorption coefficient and a normalized lineshape function used previously to model the fundamental vibrational transition of O_2–O_2 spectra (*16*) to synthesize the spectrum. The results are presented in Fig. 1 for $T = 296$ K. The calculated O_2–H_2O spectrum exhibits more structure than the recently measured (*10*) CIA spectrum for the 1.27-μm band in pure O_2. The structure arises primarily because of the larger rotational constant of H_2O compared to that of O_2 although the amount of structure is also sensitive to the choice of lineshape. Similar spectra can easily be generated for other temperatures. These results can be used in atmospheric radiative transmission codes to see if this CIA is significant. However, in order to determine the CIA more quantitatively, we require a determination of the isotropic and anisotropic matrix elements $\langle a|\alpha|X\rangle$ and $\langle a|\gamma|X\rangle$ for O_2.

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